

Geometrical Phase Transition on WO₃ Surface

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A topographical study on an ensemble of height profiles obtained from atomic force microscopy techniques on various independently grown samples of tungsten oxide WO₃ is presented by using ideas from percolation theory. We find that a continuous 'geometrical' phase transition occurs at a certain critical level-height δ_c below which an infinite island appears. By using the finite-size scaling analysis of three independent percolation observables i.e., percolation probability, percolation strength and the mean island-size, we compute some critical exponents which characterize the transition. Our results are compatible with those of long-range correlated percolation. This method can be generalized to a topographical classification of rough surface models.

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The growth of rough surfaces and interfaces with many of their scaling and universality properties has attracted the attention of statistical physicists over the last three decades¹. One of the less studied subjects is the one concerned with the topographical properties of the self-affine surfaces. In this letter, we present a systematic investigation of percolation transition on an ensemble of experimentally grown WO₃ surfaces. This gives some 'geometrical' characteristic exponents which well describe a geometrical phase transition at a certain level-height below which an infinite cluster-height (or island) appears. The results of our work are closely related to the statistical properties of the size distribution of the islands and their coastlines together with their fractal properties.

The tungsten oxide WO₃ surface is one of the most interesting metal oxides. It has been investigated extensively because for its distinctive applications such as electrochromic²⁻⁶, photochromic⁷, gas sensor⁸⁻¹⁰, photo-catalyst¹¹, and photoluminescence properties¹². Many properties of the WO₃ thin films are related to their surface structure as well as to their surface topography and statistics such as grain size and height distribution. These properties can also be affected during the growth process by either deposition method or imposing external parameters on the grown surfaces such as annealing temperature¹³.

In order to have an ensemble of WO₃ height profiles, 34 samples were independently, and under the same conditions, deposited on glass microscope slides with an area 2.5 cm × 2.5 cm using thermal evaporation method. The deposition system was evacuated to a base pressure of $\sim 4 \times 10^{-3}$ Pa. The thickness of the deposited films was chosen to be about 200 nm, and measured by stylus and optical techniques. Using atomic force microscopy (AFM) techniques, we have obtained 300 height profiles from the grown rough surfaces with resolution of 1/256 μm in the scale of 1 $\mu\text{m} \times 1 \mu\text{m}$ (an example is shown in Fig. 1). The AFM scans were performed in various non-overlapping domains (10 images from each sample) from the centric region of the deposited samples in order for the profiles to be statistically independent.

The percolation problem^{14,15} is an example of the simplest pure geometrical phase transitions with nontrivial critical behavior, and it is closely related to the surface topography. Let us suppose a sample of height profile $\{h(\mathbf{r})\}$ is a topographical landscape. Now, let us imagine flooding this landscape and coloring the parts above the water level white and the rest black. If the water level is high, there will be small disconnected islands, while if it is low, there will be disconnected lakes. There is however a critical value of the sea level for which there is one large supercontinent and one large ocean. As long as the original height profile has a gaussian distribution with only short-range correlations, it is believed that the large-scale properties of the coastlines correspond to standard percolation cluster boundaries and thus should be described by the theory of Schramm-Loewner evolution (SLE)¹⁶ (see¹⁷ for a review of SLE). However, the height profiles of WO₃ surface are quite different due to the relevant contribution of long-range correlations¹⁸. Hence, the corresponding coastlines of the height profiles belong statistically to a different universality class¹⁹.

To define islands on a WO₃ surface, a cut is made at a certain height $h_\delta = \langle h(\mathbf{r}) \rangle + \delta \sqrt{\langle [h(\mathbf{r}) - \langle h(\mathbf{r}) \rangle]^2 \rangle} := 0$, where the symbol $\langle \dots \rangle$ denotes spatial averaging. Each island (cluster-height) is then defined as a set of nearest-neighbor connected sites of positive height. We show that there is a critical level height denoted by the dimensionless parameter

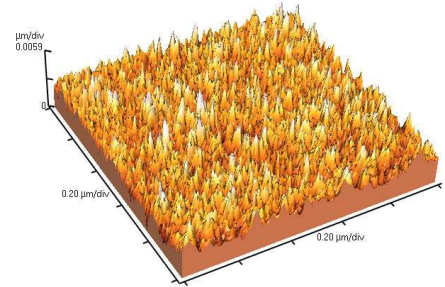


FIG. 1. (Color online) AFM image of WO₃ thin film in scale 1 $\mu\text{m} \times 1 \mu\text{m}$ with resolution of 1/256 μm .

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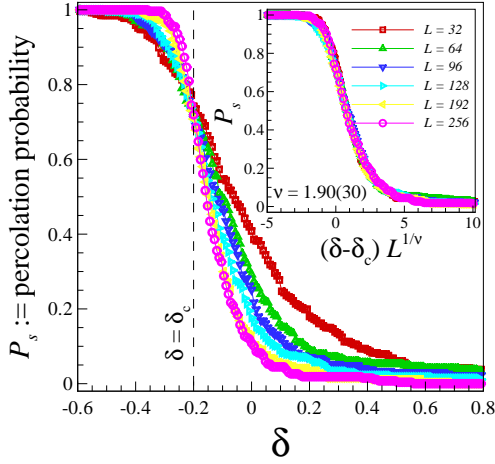


FIG. 2. (Color online) Main: probability P_s for the presence of a spanning island as a function of δ measured for different lattice sizes L . The curves cross at a critical level height $\delta_c = -0.20(1)$. Inset: data collapse for the P_s curves of different L with $\nu = 1.90$ and $\delta_c = -0.20$.

$\delta = \delta_c$, at which a continuous percolation transition occurs.

To study the finite-size scaling (FSS) properties and measure percolation observables which characterize the critical behavior, we consider a box of dynamic size $L \times L$ from the centric region of each original AFM sample. For each lattice size $16 \leq L \leq 256$, each percolation observable was averaged over all number of AFM samples.

The first quantity we measure is the probability P_s that at each level height δ , an infinite island spans two opposite boundaries of the box in just a specific direction, say y -direction. Ideally, the curves obtained for different lattice sizes cross at a single point, marking the critical level height δ_c . As shown in Fig. 2, the measured curves cross at $\delta = \delta_c$, implying that the scaling dimension of the percolation probability P_s is zero.

According to scaling theory²⁰, one expects that all the measured curves should obey the scaling form

$$P_s(\delta) = P_s[(\delta - \delta_c)L^{1/\nu}], \quad (1)$$

where the exponent ν characterizes the divergence of the correlation length ξ (proportional to the spatial extent of the islands) near the percolation threshold, $\xi \sim |\delta - \delta_c|^{-\nu}$.

We measure the values of the exponent ν and the crossing point of the curves δ_c by utilizing the data collapse. The quality of the collapse of the curves is measured by defining a function $S(\nu, \delta)$ of the chosen values ν and δ (the smaller S is indicative of a better quality of the collapse – see^{21,22} and the appendix of²³). We find its minimum $S_{min} \sim 1.78$ for $\nu = 1.90(30)$ and $\delta_c = -0.20(1)$. Inset of Fig. 2 illustrates the collapse of all the P_s curves, within the achieved accuracy, onto a universal function by using the estimated values for ν and δ_c .

Percolation strength P_∞ , which measures the probability that a point on a level height δ belongs to the largest island (or equivalently, the fraction of sites in the largest cluster), is

another quantity defined as order parameter in the percolation. As shown in Fig. 3, we have computed P_∞ as a function of δ . We find that the data follows the scaling form

$$P_\infty(\delta) = L^{-\tilde{\beta}} P_\infty[(\delta - \delta_c)L^{1/\nu}]. \quad (2)$$

Our best estimate for the exponent $\tilde{\beta}$ ($\tilde{\beta} = \beta/\nu$ in percolation theory) is $\tilde{\beta} = 0.12(4)$ which was obtained by optimizing the quality of the collapsed data. The data collapse is shown in the inset of Fig. 3.

Another independent observable is the mean island size

$$\chi = \frac{\sum'_s s^2 n_s}{\sum'_s s n_s}, \quad (3)$$

where n_s denotes the average number density of islands of size s , and the prime on the sums indicates the exclusion of the largest island in each measurement.

As presented in Fig. 4, the obtained curves $\chi(\delta)$ for different lattice sizes have their maximum around the critical level δ_c . We find that $\chi(\delta_c) \sim L^{\tilde{\gamma}}$ with $\tilde{\gamma} = 1.70(3)$ ($\tilde{\gamma} = \gamma/\nu$ in percolation theory) – see inset of Fig. 4(a). By using the exponents $\tilde{\gamma}$ and ν , it is possible to achieve a data collapse according to the scaling form

$$\chi(\delta) = L^{\tilde{\gamma}} \chi[(\delta - \delta_c)L^{1/\nu}], \quad (4)$$

which is shown in Fig. 4(b).

A point which remains is determination of the universality class which the observed percolation transition belongs to. The values we find for the exponents are obviously not those of short-range correlated percolation. In order to see whether they fit with long-range correlated percolation, we calculate the two-point correlation function $G(\mathbf{x}, \mathbf{x}')$ which is defined as the probability that two points of distance $r = |\mathbf{x} - \mathbf{x}'|$, at the critical level height δ_c , belong to the same island. The best fit to our data shows that G is a decreasing function of the distance with a power-law behavior $G(r) \sim r^{-\eta}$ and $\eta = 0.34(2)$.

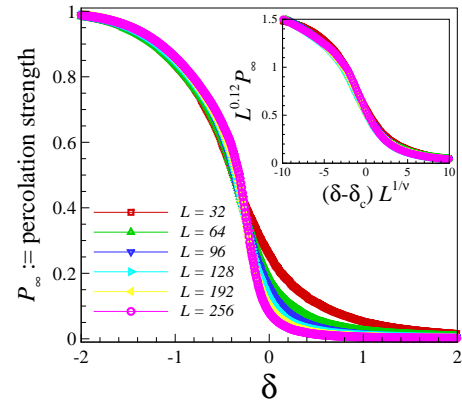


FIG. 3. (Color online) The percolation strength P_∞ of the islands as a function of δ for different lattice sizes L . Inset: collapse of the data in the suitably rescaled scales.

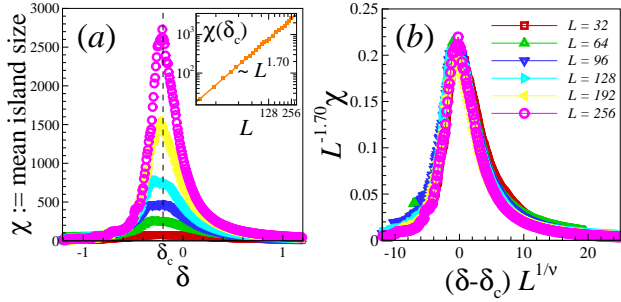


FIG. 4. (Color online) (a) mean island size χ as a function of δ for different lattice sizes L . Inset: χ at the critical level cut $\delta_c \simeq -0.20$ as a function of L . (b) data collapse for χ for different lattice sizes, according to Eq. (4).

In the past, several papers have dealt with percolation with long-range correlations^{18,24–26} in which correlations *decrease* with increasing r . A completely different percolation with long-range correlations²⁷ has also been proposed by Sahimi²⁸ in which correlations *increase* as r does²⁹. From the above references, our results are in agreement with²⁶ in which the value of ν is consistently lower than the prediction $\nu = 2/\eta$ given by¹⁸, for $\eta \leq 1$ in two dimensions.

In order to examine whether our exponents satisfy well-known scaling and hyperscaling relations, we have also computed the fractal dimension of the islands at the critical level δ_c , and found to be $d_f = 1.83(3)$. It is thus straightforward to see that our obtained exponents satisfy, within the statistical errors, the following scaling relations for $d = 2$,

$$d_f = d - \tilde{\beta} = \frac{1}{2}(d + \tilde{\gamma}) = \frac{1}{2}(d + 2 - \eta). \quad (5)$$

In conclusion, analysis of independent percolation observables on an ensemble of height profiles obtained by AFM images of WO_3 surfaces, revealed a continuous geometrical phase transition at a certain critical level height δ_c . We computed some critical exponents which can be regarded as topographical characteristics of the WO_3 surfaces. This method may lead to a topographical classification of self-affine rough surfaces by computing the exponents ν , $\tilde{\beta}$, $\tilde{\gamma}$ and η for different growth models.

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